Performance of the Savannah River Site Coulometer for Neptunium Process Accountability and Neptunium Oxide Product Characterization

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ABSTRACT

The Savannah River Site's (SRS) H-Area B-Line (HB-Line) nuclear facility is processing neptunium solutions for stabilization as an oxide. The oxide will eventually be reprocessed and fabricated into target material and the ^{237}Np irradiated to produce ^{238}Pu in support of National Aeronautics and Space Administration space program missions. As part of nuclear materials accountability, solution concentrations were measured using a high-precision controlled-potential coulometer developed and manufactured at the SRS for plutonium accountability measurements.[1] The Savannah River Site Coulometer system and measurement methodology for plutonium meets performance standards in ISO 12183-2005, "Controlled-Potential Coulometric Assay of Plutonium." [2,3,4,5] The Department of Energy (DOE) does not produce or supply a neptunium metal certified reference material, which makes qualifying a measurement method and determining accuracy and precision difficult. Testing and performance of the Savannah River Site Coulometer indicates that it can be used to measure neptunium process solutions and dissolved neptunium oxide without purification for material control and accountability purposes. Savannah River Site's Material Control and Accountability organization has accepted the method uncertainty for accountability and product characterization measurements.

INTRODUCTION

The Savannah River Site has processed a significant fraction of the nation's supply of neptunium into neptunium oxide for safer, long-term storage and for the eventual production of plutonium heat-source material for the space program. The chemical material process used to convert dissolved neptunium from an acidic solution into neptunium oxide is discussed below.

The coulometric assay methodology for neptunium and the related lessons learned in material control and accountability of neptunium during recent Savannah River Site processing campaigns have been assembled and published here in. Similar nuclear material processing efforts and analytical measurements for neptunium may not be repeated for many years. In addition, this out-year mission is not planned to occur at the Savannah River Site.

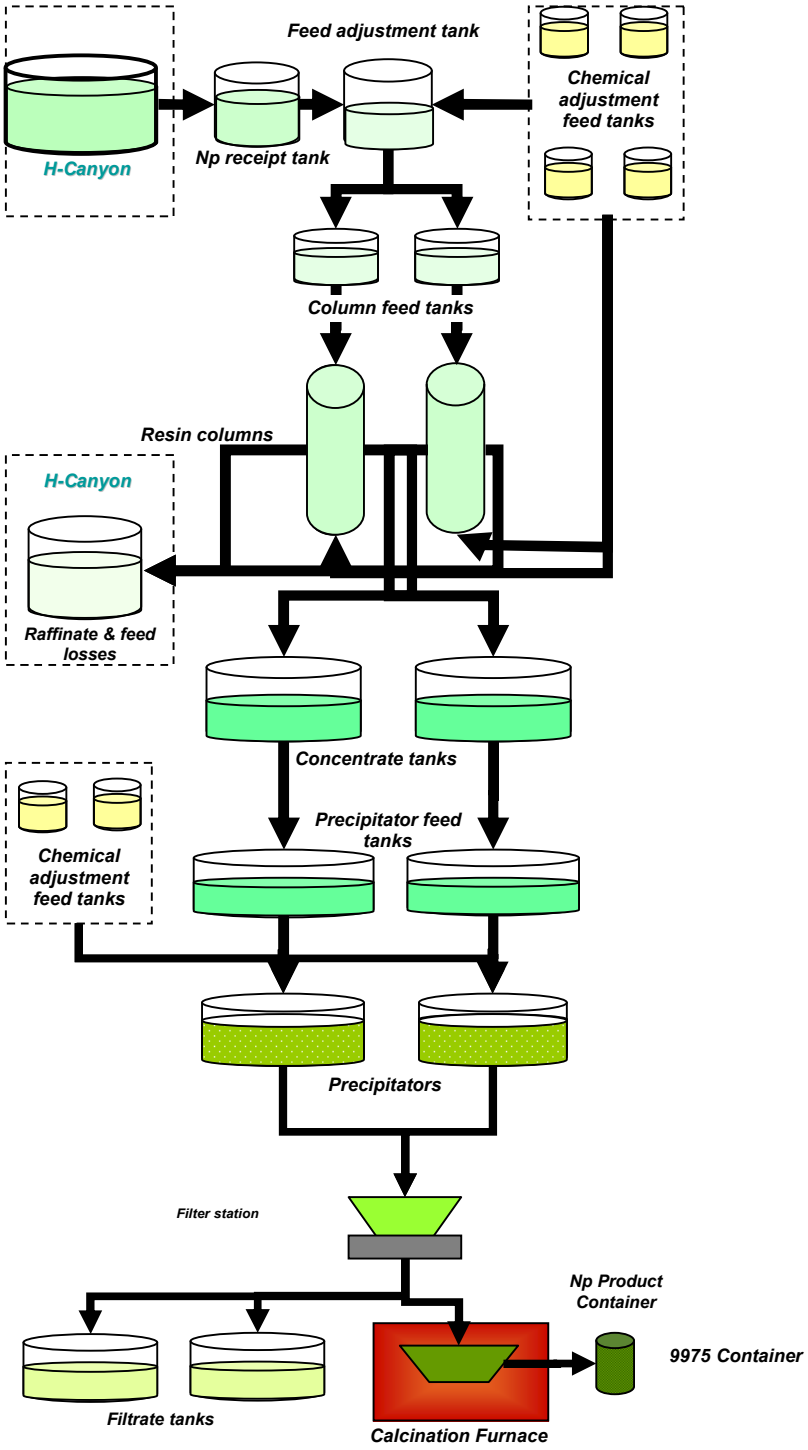
This paper addresses the issue of performing traceable neptunium accountability measurements in the absence of a U. S. certified reference material for neptunium assay as well as documenting method performance and measurement reliability.

BACKGROUND

Savannah River Site HB-Line Facility – Flowsheet for neptunium oxide production

Figure 1 displays the flowsheet for neptunium oxide production in the SRS HB-Line nuclear facility. Neptunium solution is received from the H-Area Canyon nuclear facility (H-Area Modified-PUREX process) via stream-jet transfer. The solution is then transferred to a feed adjustment tank. The acid concentration of the feed solution is adjusted to 8 M using nitric acid and the neptunium oxidation state is adjusted to Np^{4+} using ferrous sulfamate and hydrazine mononitrate. The adjusted neptunium solution is transferred to one of the column feed tanks and subsequently sent to an anion exchange column to remove contaminants, where it is rinsed with a partition wash and a decontamination wash. The neptunium is then eluted as a concentrate from the column. The neptunium is precipitated from the concentrate using oxalic acid. The slurry is filtered and the neptunium oxalate is heated to a minimum of 635°C for three hours to convert the oxalate to an oxide. The neptunium dioxide product is packaged in a 9975 storage container for storage and shipment.

Figure 1. Neptunium Oxide Flowsheet



Sample points

Prior to transferring the neptunium feed from the H-Canyon and after receipt into HB-Line, the neptunium solution is sampled and measured for accountability purposes using controlled-potential coulometry. Taking samples and measuring them for the neptunium concentration is performed throughout the process. However, the adjusted neptunium solution containing high acid, an excess of ferrous ion, and hydrazine does not lend itself to measurement by coulometry. Spectrophotometry is applied to measure the neptunium concentration at this sample point and also on samples from column raffinate and filtrate waste solutions. These low-level waste solutions are also measured by alpha counting. The concentrated neptunium solution from the column purification stage is a key sample point within the process and is measured by coulometry. The neptunium dioxide product is sampled for accountability and product specification measurements including coulometry prior to transferring the oxide powder into the 9975 storage container.

Savannah River National Laboratory

The Savannah River National Laboratory (SRNL) organization performs numerous research and development functions as well as technical and engineering support functions for the SRS operations organizations, DOE-Headquarters programs, NNSA programs, Homeland Security programs, other DOE contractors, and international programs including support to the Department of State – International Safeguards Program Office (ISPO). These SRNL functions included developing, modifying, and validating process flowsheets used at the Savannah River Site. The SRNL staff developed the HB-Line neptunium flowsheet in Figure 1, and provided laboratory scale validation of its key operating parameters. SRNL staff also provided moisture and volatile impurity measurement on the HB-Line neptunium oxide product.

SRS Analytical Laboratories

The SRS Analytical Laboratories organization provides analytical measurement and services to the SRS operations and programmatic organizations. Measurement services include destructive and nondestructive measurements that support material control and accountability, nuclear criticality safety, process control, waste acceptance criteria, regulatory compliance, environmental monitoring, internal dosimetry (bioassay), and industrial hygiene measurements. The Analytical Laboratories staff collaborates with the SRNL staff and also provides technical support and measurement services to many of the same external customers that receive support from the SRNL.

Savannah River Site Coulometer

The SRS Coulometer system is based upon the original coulometer integrator and automated instrument control system designed by Thomas L. Frazzini and Michael K. Holland, DOE New Brunswick Laboratory, Argonne, Illinois.[6] The SRS Coulometer was redesigned and substantially upgraded by Joseph V. Cordaro, et al., of the SRNL's Engineered Equipment and Systems organization, working in collaboration with Michael K. Holland, et al., at the SRS Analytical Laboratories organization.[1,7]

METHODOLOGY

Traceability of neptunium measurements by controlled-potential coulometry

The SRS controlled-potential coulometric measurement method is recognized as a definitive method, traceable to the international measurement system through electrical and mass standards.[8] The methodology is typically validated and the uncertainty estimated using a traceable certified reference material, such as CRM 126 plutonium metal. For the controlled-potential coulometric measurement of plutonium using procedural standard ISO12183:2005, the Savannah River Site has consistently demonstrated a measurement uncertainty on the order of 0.1% (1-sigma), or better, using this methodology.[1,2,3,6,7,9,10]

In the absence of U.S. certified reference materials for neptunium, the Savannah River Site has developed two complementary hierarchies for validating the measurement method and estimating uncertainties:

- Comparison of SRS coulometric measurements procedures for Pu and Np
- Comparison of SRS coulometric assay results with NpO_2 stoichiometry

Comparison of SRS coulometric measurement for plutonium and neptunium

Table 1 compares and contrasts the coulometric measurement procedures and protocols for plutonium and neptunium used by the SRS Analytical Laboratories. Key parameters have been evaluated as follows:

- The International Organization for Standardization (ISO), the ASTM International, and the American National Standards Institute (ANSI) do not have a procedural standard for the coulometric assay of neptunium. However, the Savannah River Site neptunium coulometric method is modeled after the plutonium coulometric method, which is fully compliant with ISO12183:2005. Instrument calibration using electrical standards is identical. Neptunium subsamples and aliquots are taken on a mass-basis.

- Sample dissolution in acid followed by aliquot preparation on a mass-basis is very similar for both plutonium and neptunium. However, microwave digestion of the neptunium oxide produced by the Savannah River Site generated a gelatinous residue that is not observed by hot block dissolution of neptunium oxide. This observation will be discussed in additional detail, later in this paper.

- For both plutonium and neptunium, coulometric background current levels are both acceptably low. The background current integral during neptunium electrolysis is five times greater than the background current integral during the plutonium electrolysis. To compensate for the higher background current levels, the neptunium content in an aliquot was increased by a factor of three-to-four (3-4) as compared to typical plutonium aliquots. Increasing the neptunium aliquots size to correspond with the increased background current integral is seen as an action that aligns the plutonium and neptunium measurement protocols.

- For plutonium coulometric measurements, candidate materials at the Savannah River Site are typically product quality solutions and solid materials (metals and oxides) that meet applicable nuclear grade specification. Other plutonium assay and concentration measurement techniques, including isotope dilution mass spectrometry, diode array spectrophotometry, and alpha counting are applied when more appropriate for the candidate material and data quality objectives.

- Neptunium candidate materials measured by controlled-potential coulometry are diverse. In addition to the neptunium oxide product material and the neptunium product stream after anion exchange purification, coulometric measurements have been applied to the neptunium feed solution samples taken prior to the chemical adjustment and anion exchange purification performed in HB-Line.
  - The neptunium oxide product material contains 1% thorium oxide, which was not removed from the feed material during column purification. Thorium has only one stable oxidation state and does not interfere with the coulometric measurement of neptunium.
  - The neptunium feed solution contained significant levels of metallic impurities, entrained organic material, and halides.

- In both the plutonium and neptunium aliquot preparation protocols, fuming operations, oxidation state adjustments, and column purifications are designed to generate a reproducible and stable aliquot chemistry.
  - For aliquots of nuclear-grade plutonium, fuming to dryness in sulfuric acid is effective at digesting and volatizing common impurities.
  - For aliquots from Savannah River Site neptunium samples, a more aggressive fuming sequence was developed. Aliquots are triple fumed to dryness as neptunium sulfate, with each fuming started with both sulfuric and nitric acid. The combination of sulfuric and nitric acids and triple fuming to dryness proved to be adequately effective at digesting the feed solution and removing volatile impurities in preparation for coulometric measurement.
  - It was observed that the kinetics of the coulometric electrolysis steps were better for aliquots of the dissolved neptunium oxide material compared to aliquots from neptunium feed solution samples when all of the neptunium aliquots were triple fumed in the same aggressive manner. For the impure feed material, slightly elevated random uncertainty was observed. A larger coverage factor should also be applied when estimating the systematic uncertainty for coulometric measurement of the impure feed material.

- Column purifications, when applied, are effective at removing impurities. Oxidation state adjustments using chemical reducing and oxidizing agents either before column purification or sample measurement are intended to convert the plutonium or neptunium into the desired oxidation state for the purification or measurement step. Under typical conditions, neptunium and plutonium aliquots do not contain significant interfering species after these preparation steps and the oxidation state distribution of the plutonium or neptunium can be addressed by the measurement protocol.
  - Plutonium purification by anion exchange has a demonstrated recovery of 99.95^{+}%.
  - Neptunium purification by extraction chromatography has a demonstrated recovery of only 99.5^{+}%.[11]

- When plutonium aliquots are fumed to dryness in sulfuric acid, but not purified, iron is a common interference. The iron interference is quantitative and is corrected based on a separate trace iron measurement with minimal impact on plutonium measurement reliability. Refer to ISO 12183:2005 for details on this correction. Iron does not interfere in the coulometric measurement of neptunium.

- The formal potentials of the plutonium and neptunium are measured using the same procedural protocols with the same measurement reliability. Refer to ISO 12183:2005 for details on this measurement.

The only major differences in the coulometric measurement of neptunium versus plutonium involve oxidation state control during the measurement. Plutonium measurement involves red/ox measurement of the Pu^{4+}/Pu^{3+} couple. Interference from PuO_2^{2+} (Pu^{6+}) is avoided by preventing its formation during the sample preparation process. The neptunium measurement involves red/ox measurement of the NpO_2^{+2}/NpO_2^{+} (Np^{6+}/Np^{5+}) couple. Interference from Np^{4+} can not be eliminated by efforts to avoid formation of neptunium in this oxidation state, which is easily created during sample dissolution and preparation. Instead, immediately before the coulometric measurement step, cerium (IV) sulfate is added to the re-dissolved neptunium aliquot. The coulometry cell containing this aliquot is then placed in the coulometer cell assembly. The neptunium is first electrochemically oxidized and reduced several times at the routine red/ox potentials used for measurement. This sequence also reduces the excess Ce^{4+} ion. The neptunium electrolysis to quantify the neptunium assay is then performed. Together these chemical and electrochemical oxidation state adjustment steps ensure that all of the Np^{4+} has been oxidized, before the total neptunium is measured, as the NpO_2^{+}/NpO_2^{+2} couple. The integrated current for the preliminary oxidation electrolyses routinely produces results that are biased high because some of the neptunium is still present as Np^{4+}. This Np^{4+} is oxidized to NpO_2^{2+} and generates two electrons per atom of Np^{4+} versus one electron per atom for NpO_2^{+}. Once all of the neptunium is converted to NpO_2^{2+} and NpO_2^{+}, the electrolysis is believed to be 100% current efficient and the measurement of neptunium is quantitative.

The increase in the cited uncertainty for neptunium measurements versus plutonium measurements is attributed primarily to the more complicated oxidation state controls and adjustments, especially the multiple electrolysis steps required for each neptunium aliquot and to the variation in the larger background current integral for neptunium. In addition, a larger coverage factor is applied to the estimate for the systematic uncertainty of the neptunium measurement since the method has not been demonstrated on a neptunium certified reference material or by participation in a neptunium external exchange program. The uncertainties that are cited in Table I apply to the neptunium oxide produced at the Savannah River Site. Measurement of the impure feed material has a random uncertainty that was approximately 50% greater. A larger coverage factor was applied when estimating the systematic uncertainty for the feed material since it can not be demonstrated on a stoichiometric basis.

Table 1. Comparison of SRS coulometric measurements procedures for plutonium and neptunium

	Pu by CPC	Np by CPC
Procedural standard	ISO12183:2005	SRS method
Certified reference material	CRM 126 Pu metal assay & isotopic reference material	No U.S. primary Np reference material
Sample size for metal or oxide	0.5-1.0 g Pu metal or Pu oxide	0.5 g of Np oxide
Dissolution	Pu Metal: 6N HCl Pu Oxide: 12 M HNO3 – 0.1 M HF Microwave & hot block capabilities	Np Oxide: 12 M HNO3 – 0.1 M HF Hot block capability
Typical aliquot content	10-15 mg Pu	30-60 mg Np
Aliquot fuming [digestion]	1-2 times to dryness in sulfuric acid	3 times to dryness in sulfuric acid and nitric acid mixture
Column purification	Used for impure materials only. Recovery 99.95^{+}%	Not used routinely. Recovery ~99.5%
Coulometer calibration methodology	Electrical – constant current • Ohms Law & Faraday Constant	Electrical – constant current • Ohms Law & Faraday Constant
Supporting electrolyte	1 N Sulfuric Acid [typical] 0.8 N Nitric Acid [option available]	1 N Sulfuric Acid [typical] 0.8 N Nitric Acid [option available]
Background current integral measurement frequency	The coulombs of background current are measured before each Pu aliquot is measured.	The coulombs of background current are measured before each Np aliquot is measured.
Typical blank value, mC (µg)	8 mC (equivalent to ~20 µg Pu)	40 mC (equivalent to ~100 µg Np)
Control-potential adjustment technique applied	Yes	Yes
Formal potential	Pu: 0.50_0 V vs. SCE Fe: 0.43_3 V vs. SCE Fe corrected based on ICP-MS.	Np 0.84_6 V vs. SCE Fe does not interfere.
Uncertainty, 1-sigma single determination • Systematic • Random	Nuclear-grade Pu Oxide, Pu metal, and Pu product solutions 0.1%, or less 0.05-0.1%	NpO_2 Impure Np Feed 0.2% 0.3% 0.2% 0.3%

Comparison of SRS coulometric assay with NpO2 stoichiometry – Material balance calculation

Neptunium oxide produced at the Savannah River Site was characterized as follows, with results detailed in Table 2:

- Neptunium by controlled-potential coulometric assay,
- Actinide impurities by inductively coupled plasma mass spectrometry (ICP-MS),
- Metal impurities by inductively coupled plasma mass spectrometry (ICP-MS),
- Plutonium determined by alpha counting,
- Uranium determined by kinetic phosphorescence analysis (KPA),
- Volatile impurities by thermal gravimetric analysis - mass spectrometry (TGA-MS),
- Fluoride and chloride by pyrohydrolysis and ion chromatography (IC),
- Silicon was estimated based upon process knowledge.

The results from these measurements are detailed in Table 2, along with an estimate of the material balance assuming that the neptunium dioxide is stoichiometric and that the firing of the neptunium oxide in HB-Line at nominally 650 °C produced oxides of the impurity elements consistent with the stoichiometry for these impurities provided in ISO 7476, which is based on firing at 850-900 °C.[12]

The material balance agrees within 0.08% of the expected 100% recovery for this typical neptunium oxide material produced at the SRS. The total for the impurity oxides represented 1.7% of the product material, with a majority of the impurities from thorium dioxide. Assuming a relative uncertainty of ~10%, 1-sigma, in the combined measurements that generated the 1.7% total impurity oxides, the material balance would have an uncertainty of ~0.17%. The observed agreement was less than the uncertainty for the material balance process and the systematic uncertainty assigned to the neptunium coulometric measurement of 0.2%, 1-sigma.

Table 2. Evaluation of neptunium assay results based upon neptunium dioxide stoichiometry and impurity oxide content (typical product characterization results)

Analyte	Method	Result Reported by Lab	Lab Reporting Units	Conversion Factor for Oxide Basis	Results Converted to Effective g/g Basis	Oxides After Firing	Gravimetric Oxide Factor per ISO 7476	
Np	Controlled-Potential Coulometry	**86.70%**	g Np / g Oxide	1.00	0.8670	NpO2	1.135	**98.40%**
Th	ICP-MS (Actinide Method)	**9500**	ug / g Np Oxide	1.00E-06	0.0095	ThO2	1.14	**1.08%**
Pu	ICP-MS (Actinide Method) & Pu Alpha	**100**	ug / g Np	8.67E-07	0.00009	PuO2	1.13	**0.01%**
U	ICP-MS (Actinide Method) & KPA	**20**	ug / g Np	8.67E-07	0.00002	U3O8	1.18	
Am	ICP-MS (Actinide Method)	**1**	ug / g Np	8.67E-07	0.00000	AmO2	1.13	
Volatiles	TGA - Weight Loss -- SRNL	**0.20%**	Percent Loss		N/A	H2O	N/A	**0.20%**
H2O	TGA-MS -- SRNL	0.10%	Ignore for Material Balance - Use TGA-Total Wt. Loss					
Cl	Pyrohydorlysis, IC	30	Ignore for Material Balance - Use TGA-Total Wt. Loss					
F	Pyrohydorlysis, IC	30	Ignore for Material Balance - Use TGA-Total Wt. Loss					
S	ICP-AES	20	Ignore for Material Balance - Use TGA-Total Wt. Loss					
C	TICTOC	<2000	Ignore for Material Balance - Use TGA-Total Wt. Loss					
Impurity Elements	ICP-MS							
Al	ICP-MS	900	ug / g Oxide	1.00E-06	0.0009	Al2O3	1.89	**0.17%**
Ca	ICP-MS	200	ug / g Oxide	1.00E-06	0.0002	CaO	1.4	**0.03%**
Cr	ICP-MS	50	ug / g Oxide	1.00E-06	0.00005	Cr2O3	1.46	**0.01%**
Fe	ICP-MS	400	ug / g Oxide	1.00E-06	0.0004	Fe3O4	1.38	**0.06%**
K	ICP-MS	200	ug / g Oxide	1.00E-06	0.0002	K2O	1.21	**0.02%**
Mg	ICP-MS	50	ug / g Oxide	1.00E-06	0.00005	MgO	1.66	**0.01%**
Na	ICP-MS	200	ug / g Oxide	1.00E-06	0.0002	Na2O	1.35	**0.03%**
Ni	ICP-MS	200	ug / g Oxide	1.00E-06	0.0002	Ni2O3	1.4	**0.03%**
Other impurities above ICP-MS LLQ		<80	ug / g Oxide					**0.01%**
Si	Estimate (process knowledge)	100	ug / g Np Oxide	1.00E-06	0.00010	SiO2	2.14	**0.02%**
Material Balance								**100.08%**

RESULTS AND DISCUSSION

Neptunium oxide digestion and dissolution method qualification

At the Savannah River Site's Analytical Laboratories, neptunium oxide dissolution for assay and impurity element measurements had been tested using two dissolution techniques:

- Closed-vessel, microwave digestion in 12 M HNO_3 – 0.1 M HF at 190 °C for 0.5 hours.
- Open-vessel, hot-block digestion in 12 M HNO_3 – 0.1 M HF at 115 °C for 10 hours.

Both dissolution protocols involved taking at least two 0.5-gram subsamples (weighed with an accuracy of 0.2 mg, 1-sigma). Each dissolved subsample was measured in duplicate by controlled-potential coulometry.

Only the open vessel, hot-block digestion was successfully qualified for neptunium assay and impurity element measurement, except for thorium. A separate open-vessel, hot-block dissolution in 12 M HNO_3 for 16 hours is required for the measurement of thorium in neptunium oxide. The presence of HF in the digestion acid resulted in thorium recoveries that ranged from 5%-50% when measured by inductively coupled plasma mass spectrometry.

Microwave digestion had been applied successfully to a variety of plutonium and uranium bearing oxide materials (both nuclear-grade and scrap). However, when microwave digestion was applied to the neptunium oxide sample materials, small and variable quantities of gelatinous residue were observed at the bottom of Teflon™ microwave vessels. The residue materials did not dissolve with the cold, dilute nitric acid used to rinse the vessel. Visual inspection did not identify any crystals of the original neptunium oxide material. Inspection of the solution for undissolved oxide particles was part of the original dissolution method qualification protocol. In addition to visual inspection of the solution in the microwave vessel, this qualification program also involved filtering dissolved neptunium oxide sample solutions using 0.45 micron cellulose nitrate filters, then rinsing the filter media, and inspecting the filters visually. If any particles had been identified, the qualification process would have involved submitting the particles for scanning electron microscopic analysis. The gelatinous residue was also observed on the filter media when the microwave vessel was rinsed aggressively, but the rinsing process was not quantitative with respect to the residue. Scanning electron microscopic examination of the entrained gelatinous residue was not considered practical. Coulometric assay measurements on the filtrate from microwave digestion of neptunium oxide samples were typically 1% to 5% low compared to assay measurements on the filtrate from hot block digestion from the same samples of neptunium oxides.

Microwave digestion was only effective at eventually digesting the gelatinous residue if the vessel was allowed to cool, the pressure relief disk replaced, and the digestion cycle repeated at least three additional times. This level of effort, the increased potential analytical loss from excessive handling, and the time required for repeated cooling, and repeated sample manipulations to replace the pressure relief disk were not considered practical.

The microwave digestion technique was abandoned in favor of an open-vessel, hot block digestion. The hot block digestion did not produce the gelatinous residue and was successfully qualified for complete dissolution of the neptunium oxide sample material.

Visual inspection and filtration of dissolved neptunium oxide subsamples

During the beginning of the neptunium oxide campaign (after successful qualification of the hot block digestion technique), all dissolved neptunium oxide sample solutions were visually inspected in the hot block vessel and then subjected to further inspection following the filtration protocol. Complete dissolution was consistently achieved and demonstrated by inspection. The filter media was thoroughly rinsed and the sample solution was submitted for neptunium assay by controlled-potential coulometry for material control and accountability (MC&A) purposes. The authors believed that the filtration step was no longer a value-added step, once the digestion method had been qualified and applied on a routine basis, and was a likely contributor to the total propagated measurement uncertainty for the neptunium assay. The authors conducted a study of the filtration step. The experimental design is detailed below and the assay results from filtered and unfiltered subsamples are detailed in Table 3. The authors then proposed eliminating the filtration protocol in favor of visual inspection of the dissolved sample solution in the hot block vessel and in the tared centrifuge tube after the solution had been transferred for weighing. This proposal was eventually approved by the contractor's MC&A organization, with concurrence from the Department of Energy – Savannah River Operations Office's MC&A organization; after the MC&A process for the HB-Line neptunium oxide production facility established full statistical control.

Experimental design

Four neptunium oxide samples received from the HB-Line neptunium process line were subsampled and dissolved using the hot block method. All subsamples were dissolved in a nitric-hydrofluoric acid mixture on a thermostatically-controlled hot block system for 10 hours. Two subsamples from each of the four samples, designated subsamples A and B, were dissolved, inspected visually, and filtered using the MC&A approved protocols. One subsample from each of the four samples, designated subsample C, was dissolved, inspected visually, but not filtered. Each dissolved subsample was brought to volume in a tared centrifuge tube and the mass of the dissolved solution was measured. Duplicate aliquots were taken by mass from each dissolved subsample. Each aliquot was measured for neptunium content by controlled-potential coulometry and the assay results calculated. Below are the neptunium assay results and a statistical analysis for the evaluation of the filtration step.

Table 3. Evaluation of the filtration step for dissolved neptunium oxide subsamples

Sample Number	**Subsample A (wt% Np)**	**Subsample B (wt% Np)**	**A & B Avg. (wt% Np)**	**Subsample C (wt% Np)**	**Overall Avg. (wt% Np)**	**Relative Difference (%)**	**Absolute Difference (wt% Np)**
1	86.35%	86.37%	86.36%	86.61%	86.42%	-0.29%	-0.25%
2	86.24%	86.41%	86.32%	86.21%	86.29%	+0.13%	+0.11%
3	86.13%	86.30%	86.21%	86.79%	86.35%	-0.67%	-0.58%
4	86.42%	86.53%	86.47%	86.51%	86.48%	-0.04%	-0.04%
N	4	4	4	4			4
Averages	86.29%	86.40%	86.34%	86.53%			-0.19%
Std. Dev.	0.13%	0.10%	0.11%	0.24%			0.30%
F-test	Not Significant						
Calculated F	5.11	s (pooled)	0.19%				
Degrees of freedom	3,3						
t-test	Not Significant						
Calculated t	1.43						
Paired t-test	Not Significant						
Calculated t	0.32						

The measurement results were subjected to an F-test and to a paired and unpaired t-test. Neither indicated a statistical difference between the filtered and unfiltered subsamples. Due to the limited size of the data set, a small, undetected difference could exist. The best estimate for any small difference between the filtered vs. unfiltered results is the difference in the grand averages, which is about -0.2 weight percent neptunium. The observed difference is in the direction expected for the physical model of the filtration process where loss during filtering is possible.

The results from the evaluation detailed in Table 3 were further substantiated during the remainder of the first phase of the neptunium oxide campaign. Coulometric measurements of dissolved sample solutions that were not subjected to filtration were on-the-average +0.2% to +0.3% higher than the initial campaign samples that had been filtered. In addition, there was a reduction in frequency of samples where one of the two dissolved subsamples was an outlier with a low recovery.

Prior to eliminating the filtration process, repeating the subsampling, dissolving, and assay measurements for the sample with the low recovery subsample typically demonstrated that the low recovery was caused by the subsample preparation process, with the filtration step being the probable cause.

However, on several occasions when both subsamples yielded low recoveries, and additional subsamples were measured, the low recoveries were confirmed. These problems involved nonrepresentative sampling of product material; significantly elevated impurity levels; or incomplete conversion of the oxalate to a dry oxide powder. On these isolated occasions, the processing problems were investigated, root causes were identified, and effective correction actions were implemented in the nuclear material process to prevent reoccurrence.

CONCLUSIONS

The Savannah River Site Coulometer and assay methodology can be used to measure neptunium process solutions and dissolved neptunium oxide for material control and accountability, process control, and product characterization purposes in the absence of a U. S. certified reference material for the assay of neptunium. Coulometric measurement traceability for neptunium has been established based upon electrical and mass standards and correlation with coulometric measurement methodology for plutonium, which is based upon procedural standard ISO12183:2005 and validated by plutonium certified reference materials. The SRS coulometric assay method for neptunium was validated based upon full characterization of the SRS neptunium oxide product and a material balance based upon a neptunium dioxide stoichiometry. Systematic uncertainty for the neptunium oxide and purified neptunium process stream is estimated at ±0.2%, 1-sigma, or better. The systematic uncertainty for the impure neptunium process stream is estimated at ±0.3%, 1-sigma. Random uncertainty for the assay of the neptunium oxide and purified neptunium process stream is estimated based upon replicated measurement to be 0.2%, 1-sigma. The random uncertainty for the impure neptunium process stream is estimated based upon replicate measurements and test solutions to be ±0.2%, 1-sigma.

Filtration of dissolved oxide samples followed by inspection of the filtrate and the filter media are effective at validating a dissolution protocol. This process detected dissolution problems with microwave digestion of the neptunium oxide. It was also an effective tool used to validate the hot-block digestion protocol of the neptunium oxide. However, when the dissolution procedure has been validated as effective at achieving quantitative dissolution, the filtration step should be eliminated from the routine measurement procedure to eliminate random and systematic errors caused by unnecessary manipulation of the sample solution.

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REFERENCES

1. Holland, M. K., and Cordaro, J. V., 1988. U.S. Department of Energy Publication DP-1751, "An Automated Instrument for Controlled-Potential Coulometry: System Documentation.
2. Holland, M.K., Weiss, J. R., and Pietri, C. E., "Controlled Potential Coulometric Determination of Plutonium," Anal. Chem., 50, 236 (1978).
3. Holland, M. K., Weiss, J. R., and Pietri, C. E., "A Reference Method for the Determination of Plutonium Using Controlled Potential Coulometry," printed in the proceedings of the 3rd ESARDA Symposium on Safeguards and Nuclear Material Management, Karlsruhe, F. R. Germany, May 6-8, 1981.
4. ISO 12183:2005, "Controlled-Potential Coulometric Assay of Plutonium"
5. American Society for Testing and Materials. 1991. Annual Book of Standards, Volume 12.01 Nuclear Energy (I), ASTM C1108-88, "Standard Test Method for Plutonium by Controlled-Potential Coulometry."
6. Frazzini, T. L., Holland, M. K., Weiss, J. R., and Pietri, C. E., "A Digital Integrator for Controlled-Potential Coulometry," Anal. Chem. Acta, 129, 125 (1981).
7. Holland, M. K., Cordaro, J. V., Fields, T. C., and Reeves, G. E., 1998. "Automated Controlled-Potential Coulometer for the IAEA," Proceedings from the 6th International Conference on Nuclear Engineering, San Diego, California, USA.
8. Uriano, G. A. and Gravatt, C. C. "The Role of Reference Materials and Reference Methods in Chemical Analysis," SRS Critical reviews in Analytical Chemistry, p361, October 1977.
9. Holland, M. K., Cordaro, J. V., Fields, T. C., and Reeves, G. E., and Kuno, T., "SRS Controlled-Potential Coulometer," Institute of Nuclear Material Management (INMM) 40th annual meeting, July 1999.
10. Holland, M. K., Nuessle, P. R., and Nichols, S. T., unpublished work. [Measurement results from routine internal quality control standards and external exchange program standards are retained in the laboratory information management system and associated quality control monitor (LIMS-QAM).]
11. Nuessle, P. R. and Holland, M. K., unpublished work. [A technical report is in preparation.]
12. ISO 7476:2003, "Determination of uranium in uranyl nitrate solutions of nuclear grade quality – gravimetric method."